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Synthesis of 1,2-Dicarbonyl-3-enes by Hydroacylation of 1-Alkynes with Glyoxal Derivatives Using Metal–Organic Framework Cu/MOF-74 as Heterogeneous Catalyst

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A crystalline copper-based metal–organic framework Cu/MOF-74 was synthesized, and used as an efficient heterogeneous catalyst for the synthesis of 1,2-dicarbonyl-3-enes by means of the hydroacylation of 1-alkynes with glyoxal derivatives in the presence of a base. Cu/MOF-74 was found to be more catalytically active for the synthesis of 1,2-dicarbonyl-3-enes than other MOFs including $Cu_2(BDC)_2(DABCO)$, $Cu_3(BTC)_2$, Cu(BDC), $Cu_2(NDC)_2(DABCO)$, $Cu_4I_4(DABCO)_2$, Ni-MOF-74, Zn-MOF-74, $Fe_3O(BDC)_3$, In(OH)(BDC), and $Zr_6O_4(OH)_4(BDC)_6$. Cu/MOF-74 also exhibited better performance than other homogeneous copper catalysts, including $Cu(OAc)_2$, $Cu(NO_3)_2$, CuI, CuBr, CuCl, $CuCl_2$, and $CuBr_2$. The Cu/MOF catalyst was able to be recovered and reused several times without a significant degradation in catalytic activity. To the best of our knowledge, the formation of 1,2-dicarbonyl-3-enes has not previously been carried out under heterogeneous catalysis conditions.

Introduction

1,2-Dicarbonyl derivatives have attracted significant attention as important intermediates in numerous organic transformations that lead to the formation of a variety of pharmaceutical candidates and agrochemicals.[1–6] Whereas simple alkyl- and aryl-substituted 1,2-diketones can be readily prepared by the oxidation of alkynes,[7–9] the synthesis of alkenyl-substituted 1,2-diketones still remains challenging. Feng and co-workers previously reported a protocol to produce alkenyl-, alkynyl-, and aryl-substituted 1,2-diketones by utilizing treatment of benzotriazole derivatives with butyllithium and subsequent reaction with esters or acid chlorides.[10] Lo and co-workers demonstrated a ruthenium-catalyzed oxidation of alkynes to form alkenyl-substituted 1,2-diketones.[11] However, a general method for the synthesis of alkenyl-substituted 1,2-diketones still remains to be explored.[11] Hashmi and co-workers recently reported the first example of a AuCl-catalyzed synthesis of 1,2-dicarbonyl-3-enes by means of the formal hydroacylation of terminal alkynes with α-ketoaldehydes in the presence of piperidine.[12] Independently, Li and co-workers also developed a CuBr-promoted approach for the synthesis of 1,2-dicarbonyl-3-enes based on the formal hydroacylation reaction of terminal alkynes with α-carbonyl aldehydes in the presence of morpholine.[13] The transformation proceeded through three-component coupling to afford a propargylamine intermediate, and subsequently isomerized to a conjugated allenylamine intermediate.[12,13] To achieve more environmentally benign approaches towards 1,2-dicarbonyl-3-enes in terms of the ease of handling, simple workup, recyclability, and reusability, heterogeneous catalysts should be investigated for the hydroacylation reaction.

Metal–organic frameworks (MOFs), also known as porous coordination polymers, are a new generation of crystalline material consisting of coordination bonds between metal cations and multidentate organic linkers.[14–19] By combining a variety of organic linkers with many metal cations of diverse oxidation states and coordination geometries, a large number of MOFs can be produced,[20] which offers several advantages such as structural diversity, well-defined structures, high surface areas, high porosity, and the ability to tune the surface hydrophobicity/hydrophilicity.[14–19,21–24] Although the commercialization of MOFs still remains a challenge, potential applications of these sponge-like materials in many fields have been extensively explored.[14,15,25–30] MOFs as heterogeneous catalysts have recently gained significant interest from both industry and academia.[31–33] Metal cations or functional groups on the organic linkers in the framework can be used to catalyze organic transformations, thus maximizing the opportunity for high dispersion and high loading of catalytically active sites.[32,34–40] During the last few years, both carbon–carbon[41–51] and carbon–heteroatom-forming organic reactions[52–60] using MOF-based catalysts have been reported in the literature.[31–33,61,62] Among many popular MOFs, copper-based frameworks have been investigated as catalysts for a variety of organic transformations owing to their unsaturated open copper metal sites.[51,55,63–69] Herein, we wish to report the synthesis of 1,2-dicarbonyl-3-enes by means of the hydroacylation of 1-alkynes with glyoxal derivatives in the presence of morpholine as a base using a copper-based metal–organic framework Cu/MOF-74 as an efficient heterogeneous catalyst. To the best of our knowledge, the forma-

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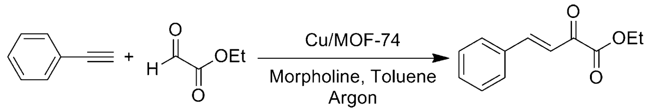
tion of 1,2-dicarbonyl-3-enes has not been previously carried out under heterogeneous catalysis conditions.

Results and Discussion

The metal–organic framework Cu/MOF-74 was synthesized according to a slightly modified literature procedure,[70] and was characterized by a variety of different techniques, including X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), thermogravimetric analysis (TGA), Fourier transform infrared (FTIR) spectroscopy, atomic absorption spectrophotometry (AAS), and nitrogen physisorption measurements (Figures S1–S7 in the Supporting Information). Cu/MOF-74 was assessed for its catalytic activity in the hydroacylation of phenylacetylene with ethyl glyoxalate to form (*E*)-ethyl 2-oxo-4-phenylbut-3-enoate as the principal product (Scheme 1). Initial studies addressed the effect of temperature on the yield of (*E*)-ethyl 2-oxo-4-phenylbut-3-enoate. In the first example of the AuCl-catalyzed synthesis of 1,2-dicarbonyl-3-enes by means of the formal hydroacylation of terminal alkynes with α-ketoaldehydes in the presence of piperidine, Hashmi and co-workers carried out the transformation at 50 °C.[12] Li and co-workers performed the CuBr-promoted hydroacylation reaction of terminal alkynes with α-carbonyl aldehydes in the presence of morpholine at 100 °C.[13] The hydroacylation reaction was carried out in toluene under argon for four hours, using two equivalents of ethyl glyoxalate and two equivalents of morpholine, at a phenylacetylene concentration of 0.5 м, in the presence of 7.5 mol% Cu/MOF-74 catalyst, at room temperature and 80, 90, 100, and 110 °C, respectively. It was observed that the transformation could not occur at room temperature, with no trace amount of product being detected after four hours. Increasing the temperature to 80 °C resulted in a 31% yield of (*E*)-ethyl 2-oxo-4-phenylbut-3-enoate after four hours. Only 40% yield was observed after four hours for the reaction carried out at 90 °C, and this value could be improved to 58% for the reaction carried out at 100 °C. Interestingly, increasing the temperature to higher than 100 °C was found to exhibit a negative impact on the reaction, with only 39% yield being detected after four hours (Figure 1).



Scheme 1. The hydroacylation of 1-alkynes with glyoxal derivatives using the Cu/MOF-74 catalyst.

For organic transformations using solid catalysts, the solvent could exhibit a significant impact on the reaction rate, depending on the nature of the catalyst.[71,72] Hashmi and co-workers previously carried out the AuCl-catalyzed hydroacylation of terminal alkynes with α-ketoaldehydes in different solvents, and pointed out that none of the other solvents was superior to toluene.[12] Li and co-workers employed several solvents for the CuBr-promoted hydroacylation reaction of terminal alkynes with α-carbonyl aldehydes, and demonstrated that 1,4-dioxane should be the solvent of choice.[13] It was therefore decided that the effect of different solvents on the hydroacylation of phenylacetylene with ethyl glyoxalate to form (*E*)-ethyl 2-oxo-4-phenylbut-3-enoate using Cu/MOF-74 catalyst should be investigated. The hydroacylation reaction was carried out at 100 °C under argon for four hours, using two equivalents of ethyl glyoxalate and two equivalents of morpholine, at a phenylacetylene concentration of 0.5 м, in the presence of 7.5 mol% Cu/MOF-74 catalyst, in toluene, 1,4-dioxane, *n*-butanol, *N*,*N*-dimethylformamide (DMF), *N*-methylpyrrolidone (NMP), dimethylacetamide (DMA), diglyme, dimethylsulfoxide (DMSO), *p*-xylene, and acetonitrile, respectively. *n*-Butanol was not suitable for the reaction, and afforded only a 6% yield after four hours. The reactions carried out in DMF and DMSO also offered low yields. Although 1,4-dioxane was previously reported to be the best solvent, it was found that only 34% yield of (*E*)-ethyl 2-oxo-4-phenylbut-3-enoate was detected after four hours for the transformation using Cu/MOF-74 catalyst. The reaction afforded 43% yield after four hours in NMP or *p*-xylene, and this value could be improved to 47% when acetonitrile was used as solvent. Among these solvents, both toluene and diglyme exhibited the best performance, with 58% yield of (*E*)-ethyl 2-oxo-4-phenylbut-3-enoate being achieved after four hours (Figure 2).

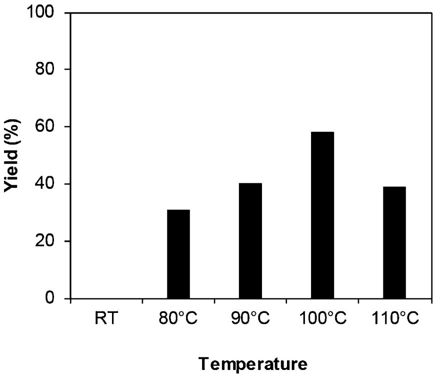


Figure 1. Effect of temperature on the reaction yield.

As mentioned earlier, the hydroacylation of phenylacetylene with ethyl glyoxalate proceeds by means of three-component coupling to afford a propargylamine intermediate, which subsequently isomerized to a conjugated allenylamine intermediate, and the hydrolyzed form (*E*)-ethyl 2-oxo-4-phenylbut-3-enoate.[12,13] The presence of a base was therefore necessary for the three-component coupling step in the catalytic cycle. Hashmi and co-workers previously employed several amines for the AuCl-catalyzed hydroacylation of terminal alkynes with α-ketoaldehydes, and reported that piperidine was the best base.[12] Li and co-workers performed the CuBr-promoted hydroacylation reaction of terminal alkynes with α-carbonyl aldehydes in the presence of different amines, and pointed out that morpholine was the base of choice.[13] It was therefore decided to investigate the effect of different bases on the formation of (*E*)-ethyl 2-oxo-4-phenylbut-3-enoate. The hydroacylation reaction was carried out in toluene at 100 °C under argon

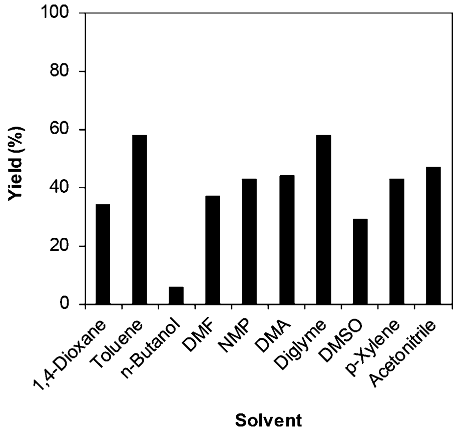


Figure 2. Effect of solvent on the reaction yield.

for four hours, using two equivalents of ethyl glyoxalate and two equivalents of the base, at a phenylacetylene concentration of 0.5 м, with 7.5 mol % Cu/MOF-74 catalyst, in the presence of morpholine, piperidine, pyridine, imidazole, cyclohexylamine, *t*BuOK, K_2CO_3, and K_3PO_4 as the base, respectively. The reaction using piperidine as the base proceeded with difficulty with only 5 % yield being detected after four hours. It was found that using pyridine resulted in 19 % yield of (*E*)-ethyl 2-oxo-4-phenylbut-3-enoate after four hours. Indeed, among these bases, morpholine exhibited the best performance, affording 58 % yield after four hours. Other bases, including, imidazole, cyclohexylamine, *t*BuOK, 1,4-diazabicyclo[2.2.2]octane (DABCO), K_2CO_3, and K_3PO_4, were found to be inactive for the transformation (Figure 3).

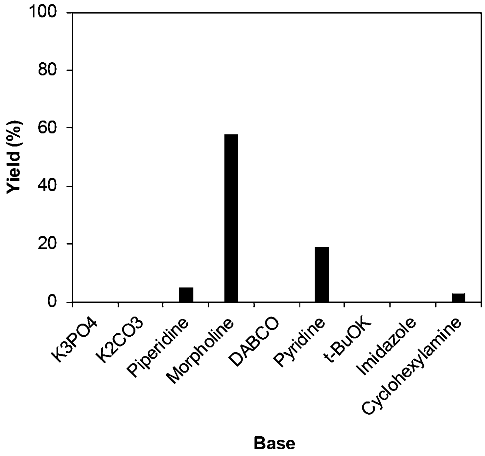


Figure 3. Effect of base on the reaction yield.

With these results in mind, we then investigated the effect of the amount of morpholine on the yield of (*E*)-ethyl 2-oxo-4-phenylbut-3-enoate. The hydroacylation reaction was carried out in toluene at 100 °C under an atmosphere of argon for four hours, using two equivalents of ethyl glyoxalate, at a phenylacetylene concentration of 0.5 м, in the presence of 7.5 mol % Cu/MOF-74 catalyst, with 0.25, 0.5, 1, 1.5, 2, 2.5, 3, and 4 equivalents of morpholine as the base, respectively. It was found that the amount of morpholine exhibited a significant effect on the reaction yield. As mentioned earlier, the reaction using two equivalents of morpholine afforded 58 % yield of (*E*)-ethyl 2-oxo-4-phenylbut-3-enoate after four hours. Increasing the amount of morpholine resulted in a significant drop in the reaction yield, with 42, 20, and 11 % yields being detected after four hours for the reaction using 2.5, 3, and 4 equivalents of morpholine as the base, respectively. It was found that decreasing the amount of morpholine led to an improvement in the reaction yield. Indeed, 66 % yield of (*E*)-ethyl 2-oxo-4-phenylbut-3-enoate was obtained after four hours for the reaction using 1.5 equivalents of morpholine. Interestingly, the reaction yield could be improved to 70 % after four hours in the presence of 0.5 equivalents of morpholine. However, using less than 0.5 equivalent of morpholine resulted in a drop in the yield of (*E*)-ethyl 2-oxo-4-phenylbut-3-enoate (Figure 4).

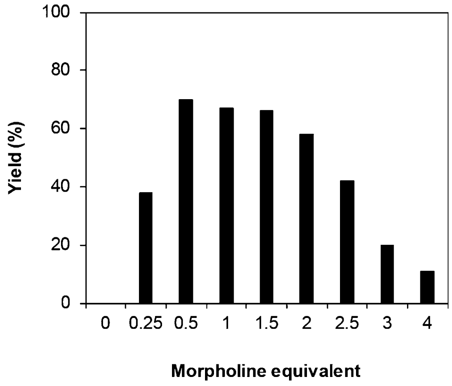


Figure 4. Effect of the morpholine amount on the reaction yield.

It should be noted that almost no reaction occurred in the absence of morpholine, which indicates the necessity of using this base for the transformation. Previously, Hashmi and co-workers used up to two equivalents of piperidine for the AuCl-catalyzed synthesis of 1,2-dicarbonyl-3-enes.[12] Li and co-workers also performed the CuBr-promoted hydroacylation reaction of terminal alkynes with α-carbonyl aldehydes in the presence of two equivalents of morpholine.[13] The fact that the amount of morpholine could be minimized for the reaction using the Cu/MOF-74 catalyst should be of advantage. Moreover, the reactant molar ratio also exhibited a significant impact on the yield of (*E*)-ethyl 2-oxo-4-phenylbut-3-enoate, and the best yield was achieved when two equivalents of ethyl glyoxalate were employed (Figure 5).

For liquid-phase organic transformations using solid catalysts, the reaction rate might be significantly affected by the reactant concentration due to the mass-transfer phenomenon. It was therefore decided to explore the impact of the reactant concentration on the yield of (*E*)-ethyl 2-oxo-4-phenylbut-3-enoate. The hydroacylation reaction was carried out in toluene at 100 °C under argon for four hours, using two equivalents of ethyl glyoxalate, with 0.5 equivalent of morpholine as the base, in the presence of 7.5 mol % Cu/MOF-74 catalyst, at phe-

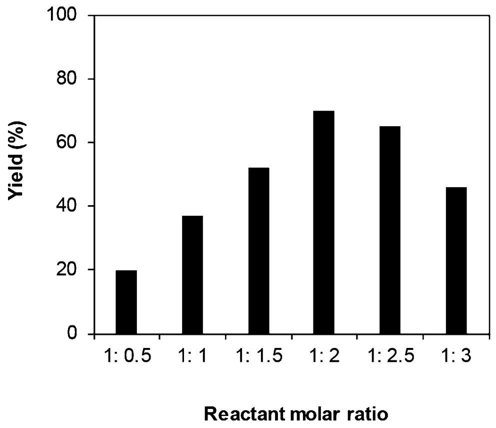


Figure 5. Effect of the phenylacetylene/ethyl glyoxalate molar ratio on the reaction yield.

nylacetylene concentrations of 0.25, 0.33, 0.4, 0.5, 0.67, 1, and 2 м, respectively. It was observed that the reactant concentration exhibited a significant impact on the formation of (*E*)-ethyl 2-oxo-4-phenylbut-3-enoate, and the best yield was observed at a phenylacetylene concentration of 0.5 м (Figure 6).

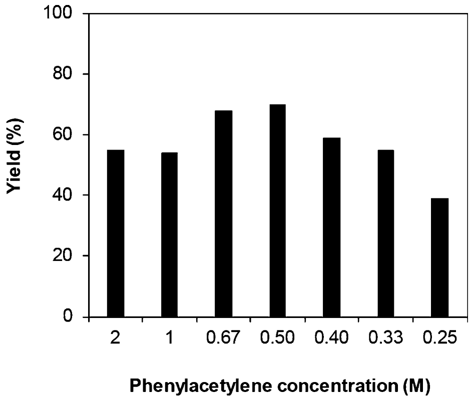


Figure 6. Effect of the phenylacetylene concentration on the reaction yield.

Another factor that exhibits a significant effect on the hydroacylation of phenylacetylene with ethyl glyoxalate to form (*E*)-ethyl 2-oxo-4-phenylbut-3-enoate using Cu/MOF-74 catalyst is the catalyst concentration. Li and co-workers previously employed up to 50 mol% CuBr catalyst for the synthesis of 1,2-dicarbonyl-3-enes based on the formal hydroacylation reaction of terminal alkynes with α-carbonyl aldehydes in the presence of morpholine.[13] The hydroacylation reaction was carried out in toluene at 100 °C under an atmosphere of argon for four hours, using two equivalents of ethyl glyoxalate, at a phenylacetylene concentration of 0.5 м, with 0.5 equivalent of morpholine as the base, in the presence of 1, 3, 5, 7.5, 10, and 12.5 mol% Cu/MOF-74 catalyst, respectively. As mentioned earlier, the reaction using 7.5 mol% catalyst afforded a 70% yield after four hours. Decreasing the catalyst concentration led to a drop in the reaction yield. Increasing the catalyst concentration to 10 mol% resulted in a 93% yield of (*E*)-ethyl 2-oxo-4-phenylbut-3-enoate being achieved after four hours. Using more than 10 mol% catalyst was found to be unnecessary as the reaction yield was not improved significantly. It should be noted that no (*E*)-ethyl 2-oxo-4-phenylbut-3-enoate was detected in the absence of the catalyst, which indicated the importance of Cu/MOF-74 for the hydroacylation of phenylacetylene with ethyl glyoxalate (Figure 7).

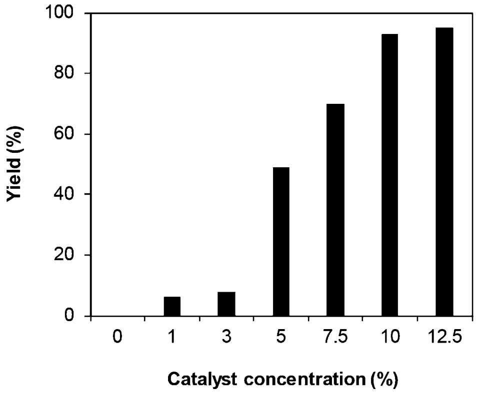


Figure 7. Effect of the catalyst concentration on the reaction yield.

Because the hydroacylation of phenylacetylene with ethyl glyoxalate to form (*E*)-ethyl 2-oxo-4-phenylbut-3-enoate using Cu/MOF-74 catalyst was performed in the liquid phase, the possibility that some of the catalytically active sites on the solid Cu/MOF could dissolve into the solution during the course of the reaction should be addressed. In several cases, owing to leaching, the transformation proceeded under both heterogeneous and homogeneous catalysis conditions.[72] To clarify whether active copper species dissolved from the solid Cu/MOF-74 catalyst contributed to the formation of (*E*)-ethyl 2-oxo-4-phenylbut-3-enoate in the hydroacylation reaction, a control experiment was carried out. The hydroacylation reaction was carried out in toluene at 100 °C under an atmosphere of argon for six hours, using two equivalents of ethyl glyoxalate, at a phenylacetylene concentration of 0.5 м, with 0.5 equivalents of morpholine as the base, in the presence of 10 mol% Cu/MOF-74 catalyst. After the first two hours of reaction time with a 38% yield of (*E*)-ethyl 2-oxo-4-phenylbut-3-enoate obtained, the Cu/MOF-74 catalyst was separated from the reaction mixture by simple centrifugation. The liquid phase was then transferred to a new reactor vessel, and stirred for an additional four hours at 100 °C with aliquots being sampled at different time intervals, and analyzed by GC. Experimental results indicated that almost no further yield of (*E*)-ethyl 2-oxo-4-phenylbut-3-enoate was observed after the Cu/MOF catalyst was removed from the reaction mixture (Figure 8). Additionally, the content of copper species in the reaction filtrate was measured using AAS. It was found that approximately 4 ppm of copper was detected in the reaction filtrate, which corresponded to 0.13% of the total amount of copper in the Cu/MOF-74 catalyst used for the transformation. It was therefore proposed that the hydroacylation of phenylacetylene with ethyl glyoxalate to form (*E*)-ethyl 2-oxo-4-phenylbut-3-enoate using the Cu/MOF-74 catalyst could only proceed in the presence of the

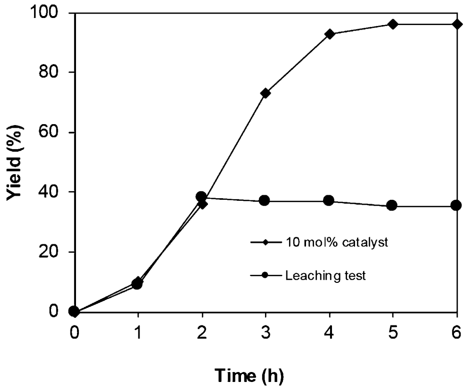


Figure 8. A leaching test indicated no contribution from homogeneous catalysis of active species leaching into the reaction solution.

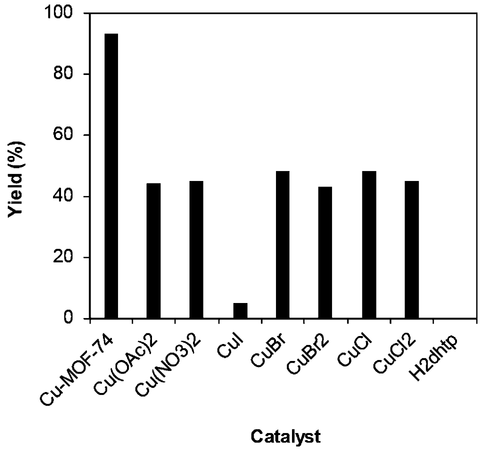


Figure 9. Different homogeneous catalysts for the hydroacylation reaction.

solid Cu/MOF catalyst, and the contribution of leached active copper species to the formation of (*E*)-ethyl 2-oxo-4-phenylbut-3-enoate, if any, was negligible.

The catalytic activity of Cu/MOF-74 in the hydroacylation of phenylacetylene with ethyl glyoxalate to form (*E*)-ethyl 2-oxo-4-phenylbut-3-enoate was also compared to that of common homogeneous copper catalysts, including $Cu(OAc)_2$, $Cu(NO_3)_2$, CuI, CuBr, CuCl, $CuCl_2$, and $CuBr_2$. The hydroacylation reaction was carried out in toluene at 100 °C under argon for four hours, using two equivalents of ethyl glyoxalate, at a phenylacetylene concentration of 0.5 м, with 0.5 equivalent of morpholine as the base, in the presence of 10 mol% copper catalyst. Previously, Li and co-workers carried out the synthesis of 1,2-dicarbonyl-3-enes based on the formal hydroacylation reaction of terminal alkynes with α-carbonyl aldehydes in the presence of morpholine, and pointed out that a high yield could be achieved when 50 mol% CuBr was used as catalyst.[13] In this study, it was found that using 10 mol% CuBr catalyst resulted in a 48% yield of (*E*)-ethyl 2-oxo-4-phenylbut-3-enoate being detected after four hours. The reaction using CuCl catalyst also proceeded with 48% yield of (*E*)-ethyl 2-oxo-4-phenylbut-3-enoate after four hours. $CuBr_2$ and $CuCl_2$ were found to be less active in the hydroacylation reaction than CuBr and CuCl, with 43 and 45% yields of (*E*)-ethyl 2-oxo-4-phenylbut-3-enoate being observed after four hours, respectively. $Cu(OAc)_2$ and $Cu(NO_3)_2$ exhibited similar activity in the hydroacylation reaction, and afforded 44 and 45% yields of (*E*)-ethyl 2-oxo-4-phenylbut-3-enoate after four hours. It should be noted that 2,5-dihydroxyterephthalic acid, the linker of Cu/MOF-74, was inactive for the transformation, with no trace amount of the desired product being detected after four hours. Interestingly, Cu/MOF-74 offered a better performance than the homogeneous copper catalyst, and produced (*E*)-ethyl 2-oxo-4-phenylbut-3-enoate in a yield of 93% after four hours (Figure 9).

To emphasize the advantages of using Cu/MOF-74 as catalyst for the hydroacylation of phenylacetylene with ethyl glyoxalate to form (*E*)-ethyl 2-oxo-4-phenylbut-3-enoate, the catalytic activity of Cu/MOF-74 was compared with that of other MOFs including $Cu_2(BDC)_2(DABCO)$, $Cu_3(BTC)_2$, Cu(BDC), $Cu_2(NDC)_2(DABCO)$, $Cu_4I_4(DABCO)_2$, Ni-MOF-74, Zn-MOF-74, $Fe_3O(BDC)_3$, In(OH)(BDC), and $Zr_6O_4(OH)_4(BDC)_6$. These MOFs were synthesized by means of a solvothermal method, and characterized according to literature procedures.[69,70,73–77] The hydroacylation reaction was carried out in toluene at 100 °C under argon for four hours, using two equivalents of ethyl glyoxalate, at a phenylacetylene concentration of 0.5 м, with 0.5 equivalent of morpholine as the base, in the presence of 10 mol% catalyst. Ni-MOF-74, Zn-MOF-74, $Fe_3O(BDC)_3$ (BDC = 1,4-benzenedicarboxylic acid), In(OH)(BDC), and $Zr_6O_4(OH)_4(BDC)_6$ were found to be inactive for the transformation, with only a trace amount of (*E*)-ethyl 2-oxo-4-phenylbut-3-enoate being detected after four hours. Although several Cu/MOFs could be used as catalyst for the hydroacylation reaction, $Cu_4I_4(DABCO)_2$ was completely inactive. The reaction using the Cu(BDC) catalyst proceeded with 45% yield of (*E*)-ethyl 2-oxo-4-phenylbut-3-enoate after four hours. $Cu_2(NDC)_2(DABCO)$ (NDC = naphthalenedicarboxylate) was observed to be more active than Cu(BDC) for the hydroacylation reaction, and afforded 53% yield after four hours. $Cu_2(BDC)_2(DABCO)$ and $Cu_3(BTC)_2$ (BTC = 1,3,5-benzenetricarboxylate) also offered similar activity, with 59 and 57% yields being obtained after four hours. Among these MOFs, it was found that Cu/MOF-74 exhibited the best performance, producing (*E*)-ethyl 2-oxo-4-phenylbut-3-enoate in a yield of 93% after four hours (Figure 10). The fact that Cu/MOF-74 gave a significantly higher activity for the transformation than several homogeneous copper catalysts and MOF-based catalysts is therefore an advantage.

To gain insights into the reaction pathway of the hydroacylation of phenylacetylene with ethyl glyoxalate to form (*E*)-ethyl 2-oxo-4-phenylbut-3-enoate using Cu/MOF-74 catalyst, some mechanistic studies were carried out. In the first experiment, the hydroacylation reaction was carried out in toluene at 100 °C under air for four hours, using two equivalents of ethyl glyoxalate, at a phenylacetylene concentration of 0.5 м, with 0.5 equivalent of morpholine as the base, in the presence of 10 mol% Cu/MOF-74 catalyst. It was observed that the transformation afforded a 44% yield of (*E*)-ethyl 2-oxo-4-phenylbut-3-enoate after four hours under air. It should be noted that the reaction carried out under argon could proceed to 93% yield of (*E*)-ethyl 2-oxo-4-phenylbut-3-enoate after four hours. In the

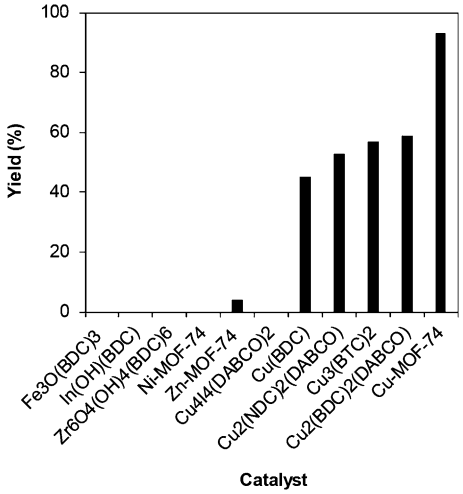


Figure 10. Different MOFs as catalyst for the hydroacylation reaction.

second experiment, the reaction was carried out under argon for two hours, producing the desired product in a yield of 38%. After that, the argon was replaced by air, and the reaction mixture was heated at 100 °C under air for a further two hours. Under these conditions, a 79% yield of (*E*)-ethyl 2-oxo-4-phenylbut-3-enoate was obtained. In a third experiment, the reaction was carried out under an argon atmosphere in the presence of water (5% by volume). It was found that the performance of the Cu/MOF-74 catalyst was significantly affected by the water, with only 18% yield of (*E*)-ethyl 2-oxo-4-phenylbut-3-enoate detected after four hours. These observations proposed that the formation of (*E*)-ethyl 2-oxo-4-phenylbut-3-enoate by means of the hydroacylation of phenylacetylene with ethyl glyoxalate using Cu/MOF-74 catalyst was not favored by the presence of air or water residue in the solvent. In the fourth experiment, the Cu/MOF-74 catalyst was soaked in pyridine as catalyst poison prior to use in the hydroacylation of phenylacetylene with ethyl glyoxalate. Under these conditions, only a 29% yield of (*E*)-ethyl 2-oxo-4-phenylbut-3-enoate was observed after four hours. This result suggested that the strong adsorption of pyridine on the copper sites in Cu/MOF-74 would deactivate the catalyst. However, further mechanistic studies would be necessary to elucidate the reaction pathway of the hydroacylation of phenylacetylene with ethyl glyoxalate to form (*E*)-ethyl 2-oxo-4-phenylbut-3-enoate using a Cu/MOF-74 catalyst.

As mentioned earlier, Cu/MOF-74 offered advantages over several homogeneous and heterogeneous catalysts in terms of catalytic activity. To emphasize the significant point of this Cu/MOF catalyst in the hydroacylation of phenylacetylene with ethyl glyoxalate to form (*E*)-ethyl 2-oxo-4-phenylbut-3-enoate, one issue that should be taken into account is the ease of separation as well as the deactivation and reusability of the Cu/MOF-74 catalyst. In the best case, the Cu/MOF catalyst can be facilely separated from the reaction mixture, and can be reused many times before it eventually deactivates completely. Cu/MOF-74 was therefore investigated for recoverability and reusability in the hydroacylation of phenylacetylene with ethyl glyoxalate to form (*E*)-ethyl 2-oxo-4-phenylbut-3-enoate over eight successive runs, by repeatedly separating the Cu/MOF catalyst from the reaction mixture, washing it, and then reusing it. The hydroacylation reaction was carried out in toluene at 100 °C under argon for four hours, using two equivalents of ethyl glyoxalate, at a phenylacetylene concentration of 0.5 M, with 0.5 equivalents of morpholine as the base, in the presence of 10 mol% Cu/MOF-74 catalyst. After the first run, the catalyst was separated from the reaction mixture by simple centrifugation, washed with copious amounts of DMF and methanol, and dried at 150 °C under vacuum for two hours. The recovered Cu/MOF-74 catalyst was then reused in further reactions under identical conditions to those of the first run. It was observed that the Cu/MOF-74 catalyst could be recovered and reused many times in the hydroacylation of phenylacetylene with ethyl glyoxalate to form (*E*)-ethyl 2-oxo-4-phenylbut-3-enoate without a significant degradation in catalytic activity. Indeed, a 91% yield of (*E*)-ethyl 2-oxo-4-phenylbut-3-enoate was still achieved in the eighth run (Figure 11). Moreover, the structure of the Cu/MOF-74 catalyst could be maintained during the course of the reaction, as indicated by the XRD (Figure 12) and FTIR (Figure 13) results of the recovered Cu/MOF-74.

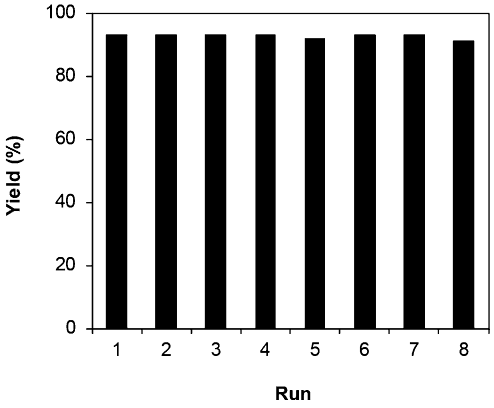


Figure 11. Catalyst recycling studies.

The study was then extended to the hydroacylation of ethyl glyoxalate with different phenylacetylenes, including phenylacetylene, 4-methoxyphenylacetylene, 4-methylphenylacetylene, 4-trifluoromethylphenylacetylene, and 4-bromophenylacetylene, respectively, in the presence of the Cu/MOF-74 catalyst (see Table 1). The hydroacylation reaction was carried out in toluene at 100 °C under an atmosphere of argon for four hours, using two equivalents of ethyl glyoxalate, at a phenylacetylene concentration of 0.5 M, with 0.5 equivalent of morpholine as the base, in the presence of 10 mol% Cu/MOF-74 catalyst. As mentioned earlier, the hydroacylation of phenylacetylene with ethyl glyoxalate could proceed to 93% GC yield of (*E*)-ethyl 2-oxo-4-phenylbut-3-enoate being obtained after four hours. The product was also purified by column chromatography (ethyl acetate/petroleum ether 1:3) to afford 90% isolated yield (entry 1), and its structure was confirmed by GC-MS and

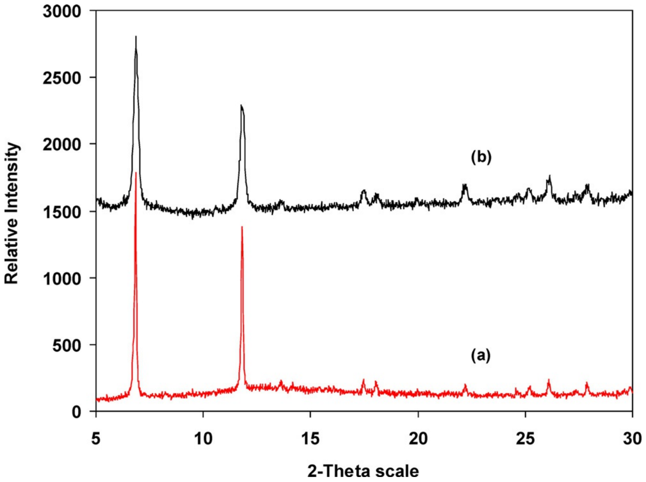


Figure 12. X-ray powder diffractograms of (a) fresh and (b) reused Cu/MOF-74 catalyst.

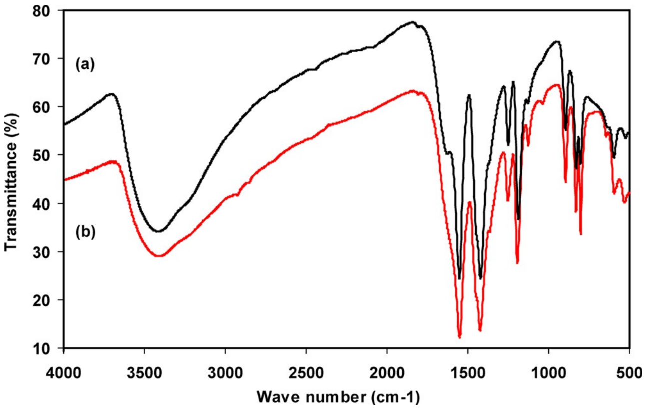


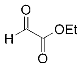
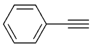
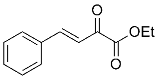
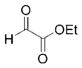
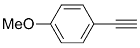
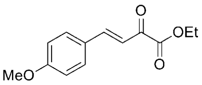
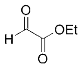
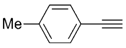
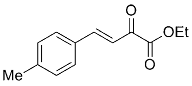
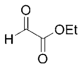
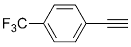
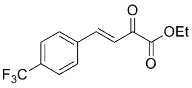
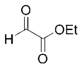
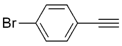
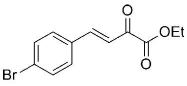
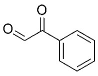
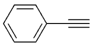
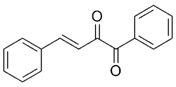
Figure 13. FTIR spectra of (a) fresh and (b) reused Cu/MOF-74 catalyst.

^{1}H and ^{13}C NMR spectroscopy. It was found that the presence of a substituent on the benzene ring in phenylacetylene resulted in a drop in the yield of the desired product. The hydroacylation of 4-methoxyphenylacetylene with ethyl glyoxalate using Cu/MOF-74 catalyst produced (*E*)-ethyl 4-(4-methoxyphenyl)-2-oxobut-3-enoate in a yield of 76 % (entry 2). By replacing 4-methoxyphenylacetylene by 4-methylphenylacetylene, the hydroacylation reaction with ethyl glyoxalate could offer 68 % yield of (*E*)-ethyl 2-oxo-4-*p*-tolylbut-3-enoate (entry 3). Using the same protocol, (*E*)-ethyl 2-oxo-4-[4-(trifluoromethyl)phenyl]but-3-enoate was obtained in a yield of 51 % (entry 4). 4-Bromophenylacetylene exhibited lower reactivity in the hydroacylation reaction with ethyl glyoxalate, affording 49 % yield of (*E*)-ethyl 4-(4-bromophenyl)-2-oxobut-3-enoate (entry 5). These observations were comparable to those previously reported by Li and co-workers in the CuBr-promoted synthesis of 1,2-dicarbonyl-3-enes based on the formal hydroacylation reaction of terminal alkynes with α-carbonyl aldehydes in the presence of morpholine.[13] Moreover, it was also found that the reaction between phenylacetylene and 2-oxo-2-phenylacetaldehyde using Cu/MOF-74 catalyst could produce (*E*)-1,4-diphenylbut-3-ene-1,2-dione in a yield of 62 % (entry 6).

Conclusion

In summary, the metal–organic framework Cu/MOF-74 was synthesized by a solvothermal method, and was characterized by a variety of different techniques including XRD, SEM, TEM, FT-IR, TGA, AAS, and nitrogen physisorption measurements. The Cu/MOF could be used as an efficient heterogeneous catalyst for the synthesis of 1,2-dicarbonyl-3-enes by means of the hydroacylation of 1-alkynes with glyoxal derivatives in the presence of a base. The nature of the base exhibited a profound impact on the formation of the desired product, and

Table 1. The hydroacylation of phenylacetylenes with glyoxalates using the Cu/MOF-74 catalyst.

Entry	Glyoxalates		Phenylacetylenes		Products		Yields [%][a]
1	**1 a**		**1 b**		**1 c**		90
2	**1 a**		**2 b**		**2 c**		76
3	**1 a**		**3 b**		**3 c**		68
4	**1 a**		**4 b**		**4 c**		51
5	**1 a**		**5 b**		**5 c**		49
6	**2 a**		**6 b**		**6 c**		62

[a] Yields of isolated products.

morpholine offered the best performance as the base for the transformation. Moreover, the amount of morpholine in the reaction mixture also significantly affected the hydroacylation reaction between 1-alkynes with glyoxal derivatives. Cu/MOF-74 exhibited higher catalytic activity for the synthesis of 1,2-dicarbonyl-3-enes than that of other MOFs including $Cu_2(BDC)_2(DABCO)$, $Cu_3(BTC)_2$, Cu(BDC), $Cu_2(NDC)_2(DABCO)$, $Cu_4I_4(DABCO)_2$, Ni-MOF-74, Zn-MOF-74, $Fe_3O(BDC)_3$, In-(OH)(BDC), and $Zr_6O_4(OH)_4(BDC)_6$. Cu/MOF-74 also offered better performance in this transformation than other homogeneous copper catalysts, including $Cu(OAc)_2$, $Cu(NO_3)_2$, CuI, CuBr, CuCl, $CuCl_2$, and $CuBr_2$. The hydroacylation reaction could only proceed in the presence of the solid Cu/MOF catalyst, and the contribution of leached active copper species to the formation of the desired product, if any, was negligible. The Cu/MOF catalyst was able to be separated from the reaction mixture by centrifugation, and could be recovered and reused several times without a significant degradation in catalytic activity.

Experimental Section

Materials and instrumentation

All reagents and starting materials were obtained commercially from Sigma–Aldrich and Merck, and were used as received without any further purification unless otherwise noted. Nitrogen physisorption measurements were conducted using a Micromeritics 2020 volumetric adsorption analyzer system. Samples were pretreated by heating under vacuum at 150 °C for 3 h. A Netzsch Thermoanalyzer STA 409 was used for TGA with a heating rate of 10 °C min^{-1} under a nitrogen atmosphere. XRD patterns were recorded using a $Cu_{K\alpha}$ radiation source on a D8 Advance Bruker powder diffractometer. Scanning electron microscopy studies were conducted on a S4800 scanning electron microscope. TEM studies were performed using a JEOL JEM 1400 transmission electron microscope at 80 kV. The Cu/MOF-74 sample was dispersed on holey carbon grids for TEM observation. Elemental analysis with AAS was performed on an AA-6800 Shimadzu. FTIR spectra were obtained on a Nicolet 6700 instrument, with samples being dispersed on potassium bromide pellets.

GC analyses were performed using a Shimadzu GC 2010-Plus equipped with a flame ionization detector (FID) and an SPB-5 column (length = 30 m, inner diameter = 0.25 mm, and film thickness = 0.25 μm). The temperature program for GC analysis held samples at 100 °C for 1 min; heated them from 100 to 280 °C at 40 °C min^{-1}; and held them at 280 °C for 4.5 min. Inlet and detector temperatures were set constant at 280 °C. Diphenyl ether was used as an internal standard to calculate the GC yield. GC-MS analyses were performed using a Shimadzu GCMS-QP2010Ultra with a ZB-5 MS column (length = 30 m, inner diameter = 0.25 mm, and film thickness = 0.25 μm). The temperature program for GC-MS analysis held samples at 50 °C for 2 min; heated samples from 50 to 280 °C at 10 °C min^{-1} and held them at 280 °C for 10 min. The inlet temperature was set constant at 280 °C. MS spectra were compared with the spectra gathered in the NIST library. The ^1H and ^{13}C NMR spectra were recorded on Bruker AV 500 spectrometers using a residual solvent peak as a reference.

Synthesis of the metal–organic framework Cu/MOF-74

In a typical preparation, a solid mixture of H_2dhtp (H_2dhtp = 2,5-dihydroxyterephthalic acid; 0.440 g, 2.22 mmol), and $Cu(NO_3)_2{\cdot}3\,H_2O$ (1.180 g, 4.88 mmol) was dissolved in a mixture of DMF (47 mL) and 2-propanol (3 mL). The suspension was stirred to achieve a homogeneous solution. The resulting solution was then distributed to six 10 mL vials. The vials were then heated at 85 °C in an isothermal oven for 18 h. After cooling the vials to room temperature, the solid product was removed by decanting with mother liquor and washed in DMF (3 × 20 mL). Solvent exchange was carried out with methanol (3 × 20 mL) at room temperature. The material was then evacuated under vacuum at 150 °C for 5 hours, yielding 0.4544 g of Cu/MOF-74 in the form of reddish black crystals (63 % based on H_2dhtp).

Catalytic studies

In a typical experiment, a mixture of phenylacetylene (0.102 g, 1.0 mmol), ethyl glyoxalate (50 % in toluene) (0.408 g, 2.0 mmol), morpholine (0.174 g, 2.0 mmol), and diphenyl ether (0.170 g, 1.0 mmol) as an internal standard in toluene (2 mL) was added into a 8 mL vial containing the pre-determined amount of Cu/MOF-74 catalyst under an argon atmosphere. The catalyst amount was calculated with respect to the copper/phenylacetylene molar ratio. The reaction mixture was stirred at 100 °C for 240 min. The reaction yield was monitored by withdrawing aliquots from the reaction mixture at different time intervals, and quenching with water (1 mL). The organic components were then extracted into ethyl acetate (3 mL), dried over anhydrous Na_2SO_4, and analyzed by GC with reference to diphenyl ether. The combined organic layers were concentrated under reduced pressure. The resulting residue was purified by column chromatography (ethyl acetate/petroleum ether 1:3) to afford (*E*)-ethyl 2-oxo-4-phenylbut-3-enoate. The product identity was further confirmed by GC-MS and ^1H and ^{13}C NMR spectroscopy. To investigate the recyclability of Cu/MOF-74, the catalyst was separated from the reaction mixture by simple centrifugation, washed with copious amounts of DMF and methanol, dried at 150 °C under vacuum for 2 hours, and reused if necessary. For the leaching test, a catalytic reaction was stopped after 2 hours, analyzed by GC, and centrifuged to remove the solid catalyst. The reaction solution was then stirred for a further 4 hours. Reaction progress, if any, was monitored by GC as previously described.

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Keywords: acylation · alkynes · copper · heterogeneous catalysis · metal–organic frameworks

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